Journal of New Materials for Electrochemical Systems 14, 173-178 (2011)
© J. New Mat. Electrochem. Systems

Direct Growth of Vertically-Aligned Single-Walled Carbon Nanotubes on Conducting Substrates using Ethanol for Electrochemical Capacitor

Mohd Asyadi Azam[1,*], Akihiko Fujiwara[2] and Tatsuya Shimoda[1]

[1] School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST),
1-1 Asahidai, Nomi, Ishikawa, 923-1292 Japan
[2] Research and Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI),
1-1-1, Kouto, Sayo-cho, Sayo, Hyogo 679-5198 Japan

Received: November 15, 2010, Accepted: April 15, 2011, Available online: May 05, 2011

Abstract: *A massive growth of vertically-aligned single-walled carbon nanotubes (VA-SWCNTs) from aluminum oxide (Al-O)-supported Co catalyst and high purity ethanol was performed using alcohol catalytic chemical vapor deposition (ACCVD) technique. SWCNTs with 50-μm thickness were grown on the substrates via this technique. The Al metal layer of 20 nm thickness was thermally-oxidized for the production of Al-O, and 0.5 nm cobalt (Co) thin films was used as catalyst for the CVD process. The CNT growth was optimized using* SiO_2*/Si substrates, and similar experimental condition was applied to the conducting substrates. The as-grown CNTs were characterized using Raman spectroscopy and electron microscopies for growth confirmation and for quality level investigation. Development of the catalyst nanoparticles and Al-O support layer was observed using atomic force microscopy (AFM) and transmission electron microscopy (TEM). The electrodes were fabricated using directly-grown VA-SWCNTs on SUS 310S, and were successfully used as an electrochemical capacitor. Electrochemical analysis using KOH aqueous electrolyte was performed by cyclic voltammetric (CV) and galvanostatic charge-discharge measurements; a maximum 52* Fg^{-1} *specific gravimetric capacitance was obtained from the VA-SWCNT electrodes.*

Keywords: vertically-aligned SWCNTs, ACCVD, direct growth method, conducting substrates, electrochemical capacitor

1. INTRODUCTION

Nanostructured carbon materials such as carbon nanotube (CNT) are theoretically known to possess abilities and remarkable properties for use as electrodes in electrochemical capacitors [1]. In particular, single-walled CNTs (SWCNTs) were experimentally proved to have a very high specific area value after a simple treatment (controlled slow oxidization), and are well suited to the requirements of electrochemical devices [2]. Furthermore, well-organized or aligned CNT arrays on substrates offer advantages for a wide variety of important applications, compared to those with random and/or entangled form of CNT that require modification or adjustment. Various methods, including the chemical vapor deposition (CVD) have been developed to grow vertically-aligned CNTs (VA-CNTs). Among them the alcohol catalytic CVD (ACCVD) technique [3] is a promising one, which is well-known for its economical merit, wide selectivity of substrates, and for yielding the catalytic reaction to grow the CNTs.

However, in applications of energy storage devices, especially electrochemical capacitors, it is desirable to directly grow the CNTs onto conducting substrates to prepare the electrodes. The metal alloy substrate/foil can directly act as a current collector in a capacitor; this simplifies the conventional electrode assembly process which is typically associated with active materials composed of conductive and adhesive additive on the current collector [4]. The direct growth method can reduce the number of process steps in fabricating the device, and also might avoid binder material incorporation (which could increase the internal resistance of the electrochemical device, thus negatively affecting capacitance performance).

In this paper, we report our research work on growing VA-SWCNTs onto SiO_2/Si and metal alloy substrates using the ACCVD technique, to fabricate electrode for the electrochemical capacitors. Cyclic voltammetric (CV) and galvanostatic charge-

---

*To whom correspondence should be addressed: Email: asyadi@jaist.ac.jp
Phone: +81-761-51-1553, Fax.: +81-761-51-1149

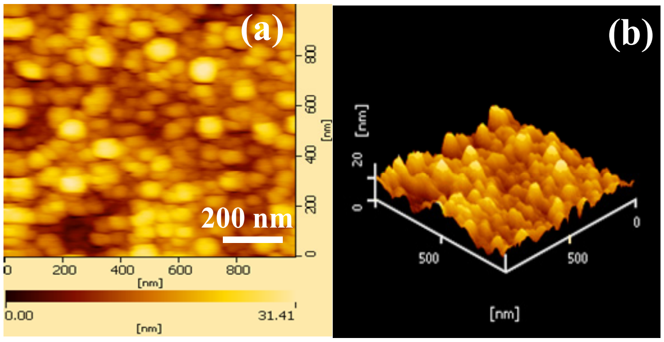

Figure 1. (Color online) (a) AFM topography image of Al-O surface just before CVD growth process. (b) 3-dimensional image of same sample at same surface position.

discharge measurements were performed to study the electrochemical performance of the fabricated VA-SWCNT-based capacitor.

2. EXPERIMENTAL

SWCNTs were grown on Al-O-supported Co catalyst thin films using ethanol in the ACCVD technique. Silicon wafer with a 400-nm-thick thermally-oxidized SiO_2 layer was used as the substrate for CNT growth parameter optimization. For conducting substrate to be used as current collectors in electrochemical capacitors, SUS 310S foil with 0.2 mm thickness were cut into 15 mm diameter round substrates. For both Al (20 nm), and Co (0.5 nm), thin films were deposited on the substrates by electron-beam deposition. For the formation of Al-O, deposited Al was first naturally-oxidized at room temperature for 2 hours. The substrate was subsequently transferred to an ultra-high-vacuum CVD furnace (an electrical furnace; MILA-3000), and baked at 400 °C in static air for 10 min just before the CVD growth process. The furnace was then evacuated using an oil-free scroll pump to around 0.1 Pa. Ar/H_2 (3% H_2) as the pretreatment gas was injected at a pressure of 400 Pa concurrently with 4 min rapid heating process of the CVD furnace. The Ar/H_2 gas was continuously flowed for another 5 min annealing process. Then, the mixed gas flow was stopped after the furnace temperature reached the CVD temperature (T) of 750 °C, and then ethanol vapor was immediately introduced into the furnace at flow rates of 110 – 130 sccm. The internal pressure of the CVD furnace during the CVD process was fixed to 3 kPa, and the CVD processing time (t) for all samples was set to 10 min.

The CNTs were grown uniformly on the 1.75 cm^2 area of the round foil. After the CVD process, the average gross weight increase of a foil with as-grown CNTs was 0.25 mg. We used a Mettler Toledo balance with an accuracy of 0.01 mg to weigh the sample. Through similar heat treatment at the same temperature without ethanol, namely, CVD process without ethanol, the foil`s weight increased 0.05 mg. Therefore, the net amount of CNT (0.20 mg) was obtained by subtraction of the weight increase of the foil with Co/Al-O films only, and those with CNTs. The SWCNTs grown were characterized using Raman spectroscopy (Tokyo Instruments; Nanofinder 30) with HeNe excitation laser (l = 632.8 nm), scanning electron microscopy (SEM; Hitachi S-4100), and high resolution transmission electron microscopy (HR-TEM; Hitachi H-9000NAR, 300 kV). The morphology analyses of Al-O and Co catalyst were studied using atomic force microscopy (AFM) and HR-TEM. Electrochemical capacitor was fabricated from a 2-electrode cell using 25-µm polypropylene (PP; Celgard) as separator. 6 M KOH aqueous solution was used as electrolyte, and the CV measurements were conducted from 0.0 to 0.7 V potential by electrochemical quartz crystal microbalances (model 420A; ALS/CH Instruments). The charge-discharge analysis was carried out using Hokuto Denko Galvanostat model HA-151. The current densities were set to 5, 10, and 25 A g^{-1}.

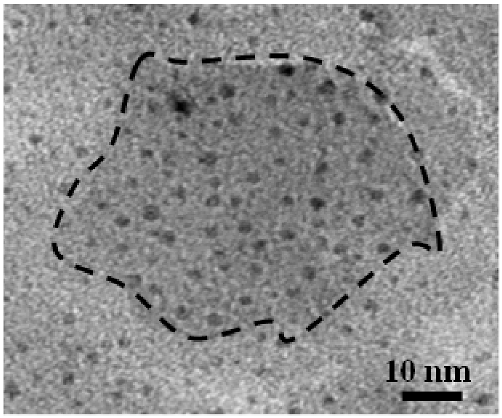

Figure 2. Cross-sectional image of HR-TEM of Al-O surface showing the Co catalyst nanoparticle crowding effect inside Al-O porous area.

3. RESULTS AND DISCUSSION

Incorporation of a buffer or oxide layer between the Si substrate and the metal catalyst (which has been reported elsewhere) can enhance catalyst activity and lifetime [5]. For the case of Al-O, this can be attributed to the increase of catalyst nucleation sites, which realizes a higher catalyst density due to surface roughness and porosity [6]. Figure 1 (a, b) shows the AFM image of Al-O particles after thermal oxidation and annealing with Ar/H_2 (just before the CVD process). The porous structure and the surface roughness (root mean square, RMS: 3.84 nm) of Al-O were confirmed. In catalyzed CNT growth, Al-O can interact both physically and chemically with the catalyst nanoparticles [7, 8]. Al-O films enhance dispersion of the formed Co nanoparticles by physically holding the nanoparticle inside the pores. In addition to this physical effect, Al-O films also interact chemically with the catalyst nanoparticles and dramatically enhance its catalytic activity by altering electronic structure of the nanoparticles [9]. The TEM image in Figure 2 confirmed this phenomenon; the Co nanoparticles crowded inside the Al-O 45 nm diameter porous area. The sample used for TEM observation was fabricated using the same steps as the one shown in Figure 1.

Figure 3 shows the AFM image of Co catalyst nanoparticles on the SiO_2 surface, without Al-O support layer. The RMS surface roughness was only 1.54 nm, far from the rough surface produced on Al-O. It is certain that the roughness came from Co nanoparticles, not from the SiO_2 surface. For well-aligned CNT growth, several research groups observed better results for catalyst nanopar-

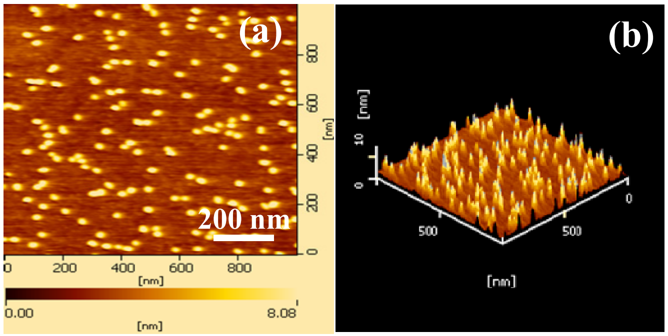

Figure 3. (Color online) (a) Co catalyst nanoparticles on SiO_2/Si substrate surface without incorporation of support layer, (b) 3-dimensional image of same sample at same surface position.

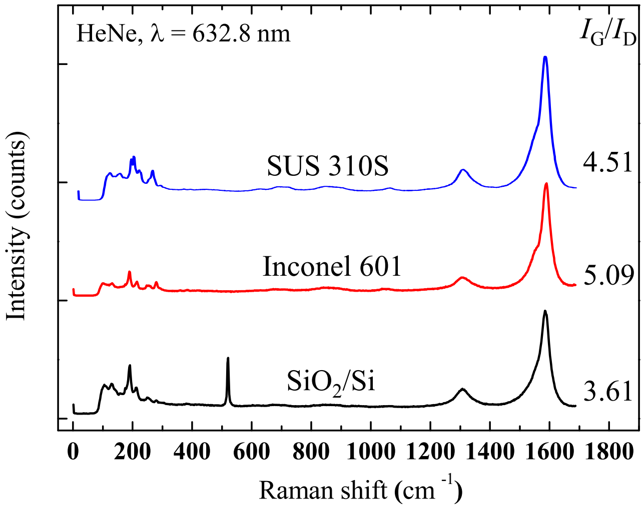

Figure 4. (Color online) Raman spectra of the vertically-grown CNTs from Co/Al-O/SiO_2/Si (black line), Co/Al-O/Inconel 601 (red line), and Co/Al-O/SUS 310S (blue line) substrates measured using HeNe laser (l = 632.8 nm). The Raman spectra and respective baselines are shifted vertically for all samples for clarity. The calculated I_G/I_D ratios of all samples are shown on the right side of the figure.

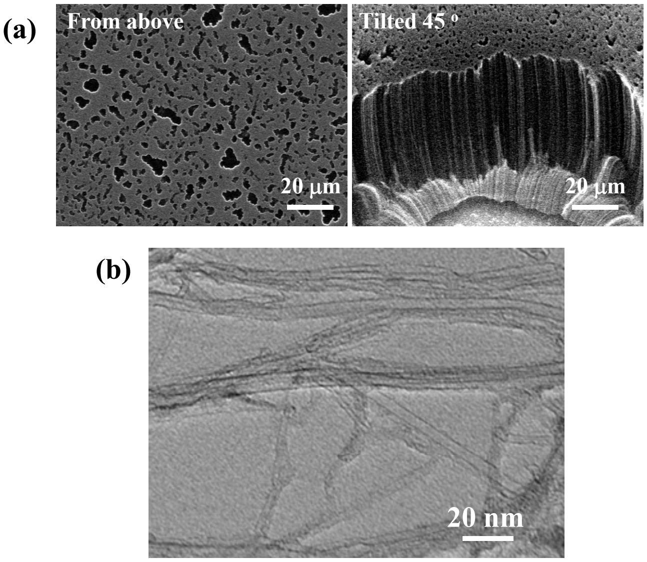

Figure 5. (a) SEM images of SWCNTs grown at t = 10 min, T = 750 °C. Left image was taken from above the substrate, and the right image was taken with tilt angle 45 °. (b) HR-TEM image of as-grown SWCNTs.

ticles on Al-O and/or Al_2O_3 than on SiO_2 [10, 11]. This is due to the flat and nonporous structure of the SiO_2 surface. For ACCVD technique, however, because of a short processing time, mostly horizontal or tangled form of CNTs would be produced on the SiO_2 surface [12]. The interactions between catalyst and support layer are found to be essential. First, the support materials partly determine the morphology of the nanoparticles and, second, they also alter the electronic structure of the nanoparticles [13], thus changing their catalytic properties. These interactions not only depend on the properties of both support and catalyst materials, but also on the surface roughness and porosity of the support materials.

Figure 4 depicts the variation of Raman spectra of CNTs on the different substrates, measured by 632.8 nm laser excitation. This figure includes Inconel 601 foil as another example of conducting substrate. The Raman spectra of all samples exhibit peaks of the radial breathing mode (RBM) from 100 to 250 cm^{-1}, which reveals the presence of SWCNTs, a D-band (defect, amorphous carbon) at approximately 1310 cm^{-1}, and a G-band (graphite, CNTs) at approximately 1590 cm^{-1} [14, 15]. This preliminary result confirmed that CNTs could also be effectively grown on metal alloy substrates using our ACCVD system. As for the quality of the as-grown VA-SWCNTs, the G-band to D-band peak intensity ratios, I_G/I_D, for all samples are also shown inside the figure. The I_G/I_D ratios of CNTs on the SUS 310S and Inconel 601 are considered almost similar to that on the SiO_2/Si substrate. Although the substrates are different, the VA-SWCNTs grown on them present similar morphologies and microstructures. This indicates that the properties of VA-SWCNTs can be mainly determined by CVD parameters and the properties of Al-O support layers, not by the substrate properties.

The SEM and HR-TEM images of the SWCNTs grown on SiO_2/Si substrate are shown in Figure 5. Similar morphology was confirmed as those on Inconel 601 and SUS 310S. Observations were made directly from above the substrate, and at a tilt angle of 45 °, to confirm the vertical structure of the CNT forest on the substrates. Most of the areas on the substrates were covered by the vertical growth of SWCNTs. Tangled “spaghetti-like” films on the substrate, indicating the horizontal growth of SWCNTs was also observed in some very limited regions, but it was not predominant, in contrast to the vertical growth of SWCNTs. HR-TEM image shows the good quality and high purity of as-grown SWCNTs. Other than the Raman analysis in Figure 4, here, it was again confirmed that the as-grown CNTs were mainly single-walled. Also, mesoporosity of CNTs is essential for ion transportation [1]. Unlike the irregular pore structures of randomly-entangled CNTs, the VA-CNTs provide a more mesoporous and more accessible surface. This translates to high electrolyte accessibility and a large effective

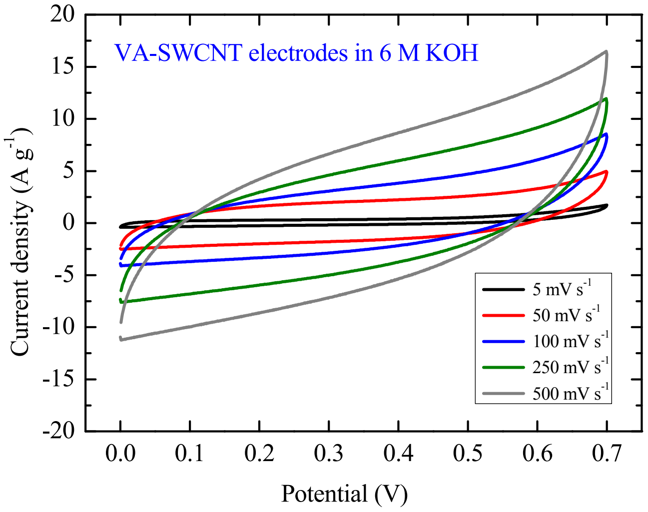

Figure 6. (Color online) CV curves of VA-SWCNT electrochemical capacitor measured at 5, 50, 100, 250, 500 mV s^{-1} scan rates. CV measurements were performed using 6 M KOH as electrolyte, in a 2-electrode-type EDLC cell. Performances of the capacitors are based on the mass per electrode of the CNTs grown during the CVD process.

surface area for the VA-CNTs, and thus a strong capacitance behavior for the CNTs electrode in the electrochemical device [16].

Figure 6 shows the result of CV measurements for an electrochemical capacitor made of VA-SWCNT grown on the SUS 310S. The electrodes were measured at 5, 50, 100, 250, and 500 mV s^{-1} scan rates within the potential range from 0.0 to 0.7 V. The CV curves confirmed the capacitance behavior of VA-SWCNTs when used as electrode material in the capacitor. Regardless of the scan rates, all of the CVs showed typical double-layer capacitance behavior. From integral calculation of the CVs, VA-SWCNT electrodes resulted in specific gravimetric capacitance (C_{sp}) of 52 F g^{-1} at 5 mV s^{-1} scan rate. The capacitances were based on the linear dependence of capacitance to the cell potential [17]. To quantitatively evaluate the charge storage capacity, capacitance of the capacitor is determined by the voltammetric charges, cell potential window, and SWCNT loading [18, 19]. Considering that the shape of CV curves is not the ideal mirror-symmetry, we used integral area of CV curve divided by scan rate to represent the sum of anodic voltammetric charges (q_a) and cathodic voltammetric charges (q_c). Sensitivity of CV measurement was 0.001 V per point. The C_{sp} was calculated accurately on the basis of the following equation [19]:

$$C_{sp} = (\int_{E_1}^{E_2} i(E)dE \div 2(E_2 - E_1)m\nu \tag{1}$$

where E_1, E_2 are the cutoff potentials in CV. $i\ (E)$ is the current. $\int_{E_1}^{E_2} i(E)dE$ is the total voltammetric charges obtained by integration of positive (charge) and negative (discharge) sweeps in CV. $(E_2 - E_1)$ is the cell potential window width. m is the SWCNT mass per electrode (explained in Experimental), and ν is the scan rate. This significant result proved that the VA-SWCNTs had good electrical contact with the substrates. This can be mainly attributed to the fact that the CNTs are well-anchored to the substrates, and also indicates that the non-conductive Al-O support layer had no influence on the contact between the CNTs and the substrate [20]. On the other hand, storing energy on and/or inside the SWCNT enables the device to have high rate capability, up to 500 mV s^{-1} (Figure 7). The current density at ~ 0.35 V cell potential was also found to increase linearly with the CV scan rates. This again indicates good double-layer capacitance behavior between electrolyte ions and vertical SWCNT.

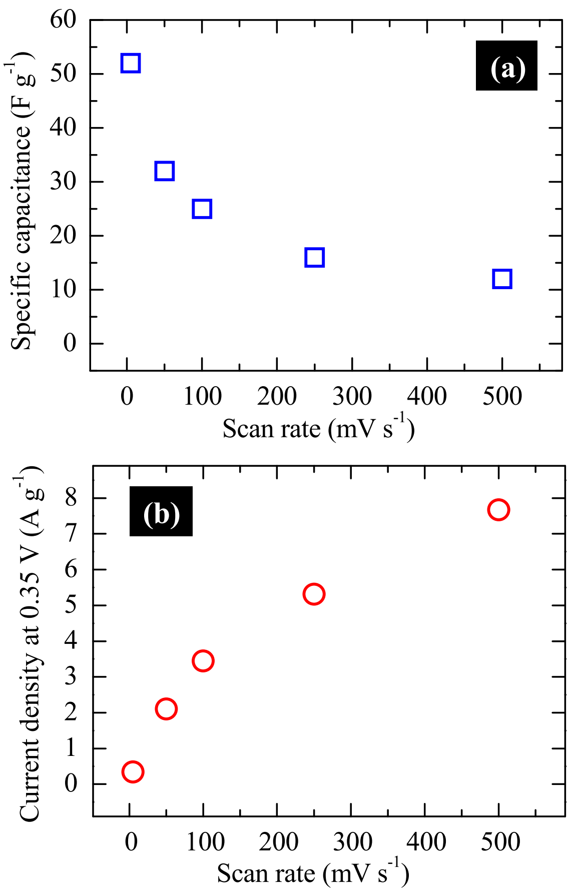

Figure 7. (Color online) (a) The plot of specific gravimetric capacitance, C_{sp} as a function of scan rate, and (b) plot showing linear dependence of the current density on the scan rate. The plot is based on the current density values at 0.35 V cell potential.

The performance of this capacitor was also evaluated using charge-discharge analysis at 5 A g^{-1} (Figure 8 (a)) from 0.0 to 0.7 V and back to 0.0 V. It was continuously measured up to (but not limited to) 10 cycles and was very stable. Various constant currents were applied to observe the ability of the electrodes to work from lower to higher current density (Figure 8 (b)). The capacitor was discharged from 0.5 to 0.2 V. The capacitor operated at very rapid (less than 1 s) charge-discharge performance, which is a well-known advantage of electrochemical capacitors [21]. Dynamic, long lifetime of a capacitor can also be expected from pure CNTs typically grown from ACCVD [22]. In a CNT-based electrochemi-

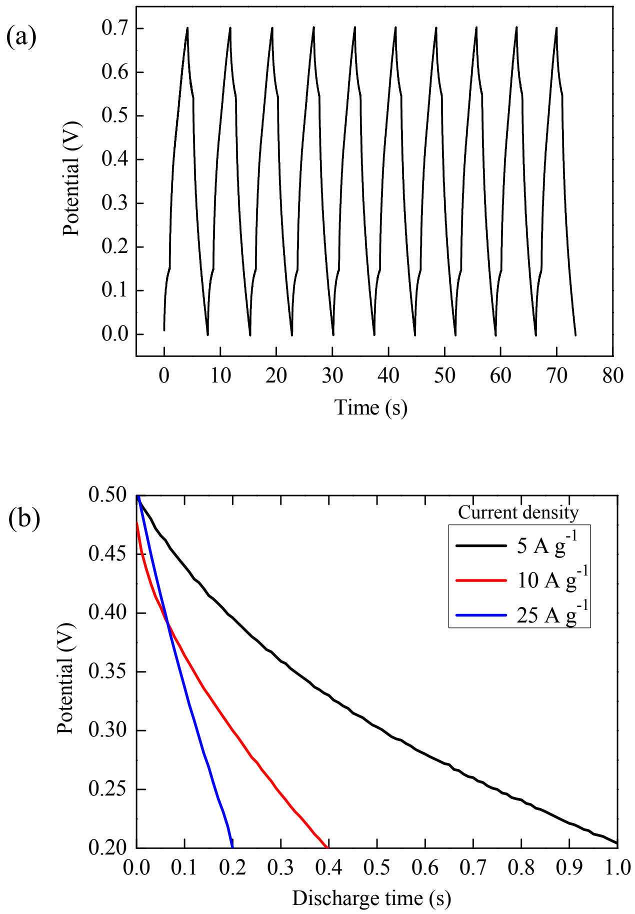

Figure 8. (Color online) (a) Galvanostatic charge-discharge of VA-SWCNT electrochemical capacitor measured at 0.0 – 0.7 V potential. The current density was fixed to 5 A g^{-1}. (b) Galvanostatic discharge at 5, 10, and 25 A g^{-1}. During this analysis, the cell was discharged from 0.5 V to 0.2 V.

cal capacitor, the ability to accumulate charge in the electrode–electrolyte interface strongly depends on ion accessibility to the outer walls and central canal of nanotubes [21]. Therefore, here, it can be suggested that the morphological structure of aligned SWCNT might open new possibilities of high performance electrochemical capacitors, whereas ion accessibility is better than that of the random or entangled growth form [23].

In order to investigate difference in capacitance performance, it is crucial to have a detailed CNT microstructure analysis before device fabrication. Future research work focusing on excellent and stable capacitors will consider several essential factors, such as alignment control, and additional treatment after the growth process. Spacing or placement between each VA-SWCNT could be performed by governing catalyst nanoparticle placement (a step before CVD). A simple treatment (thermal or oxidation) could elevate electrolyte ion accessibility to all nanotubes. As an example, a heat treatment process was reported to expand CNT surface area for ion adsorption in the bundle's interstitial channels, and/or inside the SWCNTs [24, 25].

4. CONCLUSIONS

Vertically-aligned single-walled CNTs (VA-SWCNTs) of up to 50-μm height were directly grown on electrically-conducting SUS 310S foils using ACCVD technique to fabricate SWCNT electrochemical capacitor. Similar characteristics to those grown on SiO_2/Si substrate were confirmed by TEM and Raman spectroscopy. Microscopic analyses of an Al-O support layer and Co catalyst nanoparticles were carried out accordingly, in order to understand the CNT growth mechanism. By direct growth method, end-contact between vertical SWCNTs and foils was easily prepared and also the incorporation of binder materials was avoided. Electrochemical performance of the capacitor was investigated using CV and charge-discharge analyses. From the VA-SWCNT capacitor using 6 M KOH solution as electrolyte, a maximum capacitance of 52 F g^{-1} was obtained. The capacitor also performed very well during charge-discharge measurement. The relatively good and reliable electrochemical performances can be attributed to the purity of SWCNTs grown from the ACCVD technique, appropriate morphological structures, and again, the intrinsic properties of the SWCNTs that directly connected to the foils. Thus, the SWCNT can be another promising electrode material for high performance electrochemical capacitors. Finally, further optimization of electrochemical devices such as selection of electrolytes, additional treatments, and control of alignment (spacing, bundle etc.) is urgently necessary in order to achieve better capacitance performance.

5. ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid from Japan Society for the Promotion of Science (JSPS) for Research Fellows. Part of this work was supported by Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT), Ministry of Higher Education Malaysia (MOHE) and Universiti Teknikal Malaysia Melaka (UTeM). Authors acknowledge Dr. Hiroshi Uemachi (Polythione Inc.) for sharing his expertise in electrochemistry. We are also grateful to Ms. Mary Ann Mooradian for the proof-reading and English correction of the manuscript.

REFERENCES

[1] E. Frackowiak, and F. Beguin, Carbon, 39, 937 (2001).

[2] T. Hiraoka, A. I-Najafabadi, T. Yamada, D.N. Futaba, S. Yasuda, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, and K. Hata, Adv. Func. Mater., 20, 422 (2010).

[3] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, and M. Kohno, Chem. Phys. Lett., 360, 229 (2002).

[4] L. Gao, A. Peng, Z.Y. Wang, H. Zhang, Z. Shi, Z. Gu, G. Cao, and B. Ding, Solid State Comm., 146, 380 (2008).

[5] T. de los Arcos, M.G. Garnier, P. Oelhafen, D. Mathys, J.W. Seo, C. Domingo, J.V. Garci-Ramos, and S. Sanchez-Cortes, Carbon, 42, 187 (2004).

[6] P.B. Amama, C.L. Pint, S.M. Kim, L. McJilton, K.G. Eyink, E.A., R.H. Hauge and B. Maruyama, ACS Nano, 4, 895 (2010).

[7] I. Yudanov, G. Pacchioni, K. Neyman, and N. Rosch, J. Phys. Chem., B 101, 2786 (1997).

[8] T. Borowiecki, React. Kinet, Cataly. Lett., 33, 429 (1987).

[9] R.L. Vander Wal, T.M. Ticich, and V.E. Curtis, Carbon, 39,

2277 (2001).
[10]M. Su, B. Zheng, and J. Liu, Chem. Phys. Lett., 322, 321 (2000).
[11]J.F. Colomer, G. Bister, I. Willems, Z. Kónya, A. Fonseca, G. V. Tendeloo, and J.B. Nagy, Chem. Comm., 1343 (1999).
[12]M.A. Azam, M.A. Mohamed, E. Shikoh, and A. Fujiwara, Jpn. J. App. Phys., 49, 02BA04 (2010).
[13]A.C. Dupuis, Progress in Materials Science, 50, 929 (2005).
[14]R. Saito, G. Dresselhaus and M.S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998) Chap. 10, p.183.
[15]M.S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, Phys. Rep., 409, 47 (2005).
[16]W. Lu, L. Qu, K. Henry, and L. Dai, J. Power Sources, 189, 1270 (2009).
[17]P. Kurzweil, M. Chwistek, and R. Gallay, Proc. 2nd European Symposium on Super Capacitors & Applications (ESSCAP) (2006).
[18]B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer, New York (1999).
[19]W. Chen, Z. Fan, L. Gu, X. Bao, and C. Wang, Chem. Commun., 46, 3905 (2010).
[20]H. Zhang, G.P. Cao, Z.Y. Wang, Y.S. Yang, and Z.N. Gu, Carbon, 46, 822 (2008).
[21]P. Simon, and Y. Gogotsi, Nature Mater., 7, 845 (2008).
[22]A. I-Najafabadi, S. Yasuda, K. Kobashi, T. Yamada, D.N. Futaba, H. Hatori, M. Yumura, S. Iijima, and K. Hata, Adv. Mater., 22, E235 (2010).
[23]M. Inagaki, H. Konno, and O.Tanaike, J. Power Sources, 195, 7880 (2010).
[24]A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, and Y. Achiba, Chem. Phys. Lett., 336, 205 (2001).
[25]J. Fan, M. Yudasaka, J. Miyawaki, K. Ajima, K. Murata, and S. Iijima, J. Phys. Chem., B 110, 1587 (2006).